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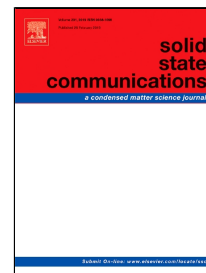
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Fluorinated perovskite as magnetic spin-polarised semiconductor

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Abstract

Much work has been done on cation substitution of manganese perovskites, but less on anion substitution. Recently there have been reports on fluorination of these compounds, generally leading to double perovskite structures. This work explores the effect of fluorine substitution on the magnetic and electrical properties of the perovskite cubic strontium manganite using first principles DFT calculations. Results on fluorine-doped strontium manganite with one or two fluoride ions surrounding each iron are presented. The ground state of $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ is found to be a small band gap spin-biased semiconductor. This is the first proposal that a fluorinated manganite could be a ferromagnetic spin-polarised semiconductor.

A. perovskites ; D. ferromagnetism ; A. semiconductors ; E. DFT

1. Introduction

Ferromagnetic semiconductors are the subject of much interest for use in spintronic devices. Recently, a number of transition-metal doped semiconductors [for example 1- 8] and doped mixed oxides [for example 9 - 12] have been identified often as thin films. However these materials used metals as dopants. We suggest here that such materials can be produced via anion-doping. Following work on SrFeO_2F [13], we set out to calculate properties of fluorinated SrMnO_3 . For the analogous compound SrMnO_2F , we found that the ground state was a G-type antiferromagnetic material. However our original interest was in the mixed oxidation state fluorinated strontium manganite, $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ ($\text{SrMn}_{2.5}\text{F}_{0.5}$) as a potential colossal magnetoresistance (CMR) material. This possibility had led Lobanov et al [14] to synthesise the compound $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ arguing that it should be possible to produce a material with CMR by doping strontium manganite with fluorine. This had a simple perovskite structure with Jahn-Teller distorted MnO_6 octahedra elongated along the c axis but the researchers were unable to distinguish whether the fluoride ions occupied the apical or equatorial sites. Some ferromagnetism was detected but it was not possible to assign this definitely to the oxyfluoride and it was not possible to determine whether it had CMR properties. A later paper

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reported the preparation of $\text{Sr}_2\text{MnGaO}_{5-x}\text{F}_{1+x}$ [15] as a possible CMR candidate. With $x = 0.22$, the structure was found to be layered with both Mn and Ga in octahedral environments. The F atoms occupied equatorial positions around Ga. Since then there have been a number of papers reporting the results of fluorinating strontium manganite, for example Greaves et al[16] treated $\text{Sr}_2\text{MnO}_{3.5+x}$, and $\text{Sr}_3\text{Mn}_2\text{O}_6$ with fluorine gas. For high levels of fluorination, fluorine displaced oxygen from apical positions into equatorial vacancies. Lower levels of fluorination retained the defect structure. It was noted that the samples studied contained some areas of lower fluorine content. Fluorination of $\text{Sr}_3\text{Mn}_2\text{O}_6$ led to fluorine filling equatorial vacancies and interstitial sites. Tsujimoto et al[17] prepared $\text{Sr}_2\text{MnO}_3\text{F}$ and showed that this had a Ruddleson-Popper type structure with Mn occupying an octahedral environment of 5 O atoms and 1 F. It was suggested that F occupied an apical position in a random manner. Kovba and Skolis[18] studied the phase diagram of the $\text{SrO-SrF}_2\text{-Mn}_2\text{O}_3\text{-O}_2$ and reported Gibbs energy data for the formation of $\text{Sr}_{2.5}\text{Mn}_6\text{O}_{12.5-6}\text{F}_2$. Most recently Wang et al[19] prepared thin films of $\text{SrMnO}_{3-\delta}\text{F}_\gamma$ by the action of fluoropolymers on $\text{SrMnO}_{2.5}$. Both X-ray absorption spectroscopy and DFT calculations supported the substitution of F for O rather than F filling vacant lattice sites and that the nominal oxidation state of Mn was reduced from the original +3.

In this paper, we use density functional theory (DFT) calculations to study the fluorine-doped strontium manganite, $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ which is expected to be a mixed oxidation state ($\text{Mn}^{3+}/\text{Mn}^{4+}$) material. In particular we consider the structure of the unit cell and predict the magnetism and the electronic band structure.

2. Methods

We used CRYSTAL09[20,21] and CRYSTAL14[22] for our calculations. Density functional theory (DFT) was used with the hybrid functional B3LYP[23,24]. This functional has been shown to perform well for transition metal oxides. Other newer functionals, PBE0SOL[25, 26], PWGGA/PW91[27] and B3LYP with different percentages of Hartree-Fock exchange were investigated but showed no advantage over B3LYP.

The basis sets used were all-electron sets on Mn (86-411d41)[28], O(8-411-d1)[29] and F(7-311)[30]. A pseudopotential basis set[31] was used for Sr to reduce the computer resource needed. These basis sets and the B3LYP functional were applied to SrMnO_3 and gave an optimised structure and G-type antiferromagnetic ground state in agreement with experiment. The unit cells used as the starting point in the calculation were $1 \times 1 \times 2$ supercells of the experimental unit cell of cubic SrMnO_3 . Two model structures were explored. The most obvious way to replace one oxide ion is to form a structure in which each manganese is surrounded by five oxide ions and one fluoride ion. We label this model A. An alternative, model B, has F-Mn-F chains running through the solid with one manganese surrounded by six oxide ions and the other surrounded by four oxide and two fluoride ions. Thus manganese ions in alternate layers are in environments resembling SrMnO_3 (Mn^{4+}) and resembling SrMnO_2F (Mn^{3+}). The positions of atoms in the unit cells are shown in Figure 1. These were the only structures we found to result from substituting one O^{2-} by F^- in the unit cell of $\text{Sr}_2\text{Mn}_2\text{O}_6$.

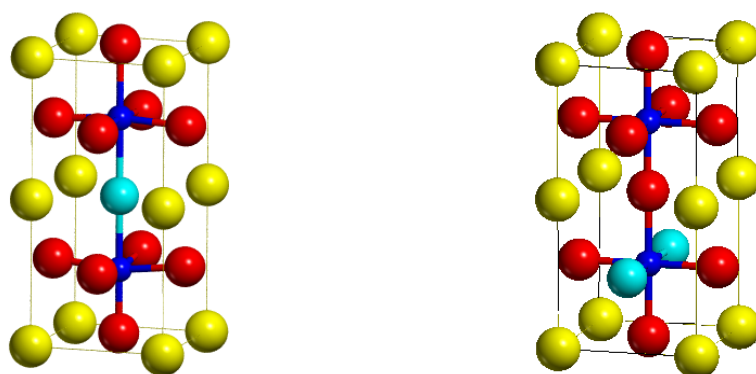


Fig. 1: (Colour on-line) Model A left and B right. In A, a fluoride ion occupies the central position of the cell as shown. In B this position is occupied by an oxide ion and there are two trans fluoride ions adjacent to the lower manganese ion. Small, dark blue spheres Mn, yellow spheres on corners and edges of the unit cell Sr, red spheres O, light blue spheres F.

Calculations with both Mn spins in the unit cell parallel (ferromagnetic) and with the spins opposed (ferrimagnetic) were performed. All structures were optimised.

3. Results

For both models we found the ferromagnetic state to be that of lower energy see Table I. Model A was found to be lower in energy than Model B.

Table 1. Calculated properties of the ferromagnetic and ferrimagnetic forms of models A and B. $1\text{\AA} = 10^{-10}\text{ m}$, $1\text{H} = 4.3597482 \times 10^{-18}\text{ J}$.

Model	Magnetism	Mulliken charges ($\alpha - \beta$)	Optimised structure (a, b, c/ \AA)	Energy/H
A	ferromagnetic	3.071, 3.684	3.830, 3.817, 8.166	- 2839.1975
A	ferrimagnetic	-2.777, 3.752	3.828, 3.828, 8.186	- 2839.1929
B	ferromagnetic	2.916, 3.764	4.002, 3.831, 7.766	- 2839.1816
B	ferrimagnetic	-2.620, 3.752	3.868, 3.833, 8.163	- 2839.1557

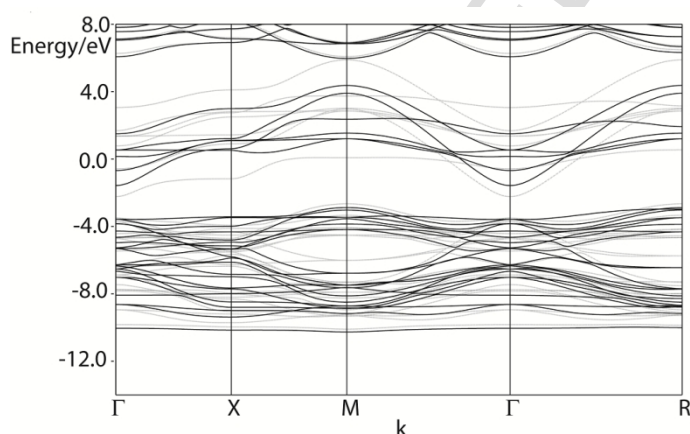
The ferromagnetic states were found to be charge ordered with a unit cell containing one Mn ion in oxidation state +4 and one Mn ion in oxidation state +3, although in the ferromagnetic form of model A, the magnetic moments (as reflected by the difference in $\alpha - \beta$ spin density) on the two manganese ions were closer than in model B. We predict that the most stable state

is the ferromagnetic state of model A. The ferrimagnetic state of model A with the spins on the Mn^{3+} ion and Mn^{4+} ion opposed was higher in energy than the ferromagnetic state by 0.125 eV. For model B the ferromagnetic state was found to be more favourable by 0.815 eV, reflecting the coupling of the electrons on Mn^{3+} and Mn^{4+} through O^{2-} in this model. Coupling through F^- would be expected to be weaker.

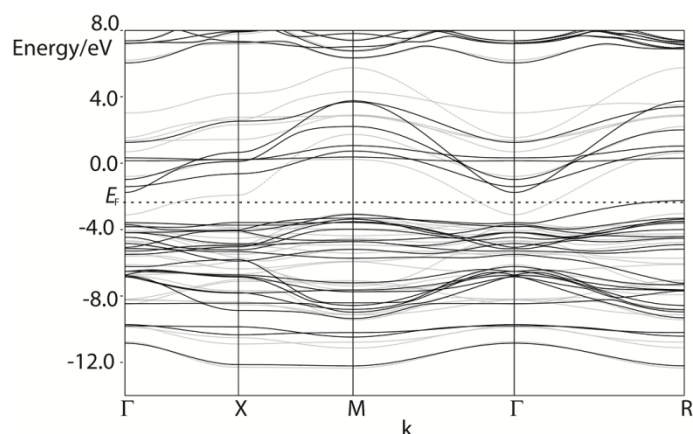
The optimised structure of model A ferromagnetic $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ had cell dimensions $a = 3.830 \text{ \AA}$, $b = 3.816 \text{ \AA}$, $c = 8.166 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. Despite the initial symmetric structure, the two manganese ions were distinguished by their oxidation states and hence the surrounding geometry in the final optimised structure. Mn^{3+} ions were surrounded by four oxide ions at 1.92 \AA , one oxide ion at 2.08 \AA and one fluoride ion at 2.21 \AA . This coordination geometry is similar to that in the recently-prepared $\text{Sr}_2\text{MnO}_3\text{F}$ [17] – Mn-O 1.90 \AA and Mn-(O/F) 2.27 \AA and indicates a Jahn-Teller distortion. Mn^{4+} ions were surrounded by four oxide ions at 1.93 \AA , one oxide ion at 1.80 \AA and one fluoride ion at 2.08 \AA . The cation-anion distances were notably shorter for Mn^{4+} . This is in line with the smaller ionic radius of Mn^{4+} relative to that of Mn^{3+} . In particular the Mn-O distance for the oxide ion *trans* to fluoride was particularly short. The experimental report[14] gave four Mn-O(F) distances of 1.903 \AA and two Mn-O(F) distances of 1.995 \AA . These distances are close to those in our model A.

Figure 2 shows the band structures of the ferromagnetic states of both models. The ferromagnetic state of model A is predicted to be a semiconductor with a small direct band gap of about 0.4 eV, comparable to that of InAs, for spins of one type at Γ (Figure 2a).

The ferromagnetic state of model B is a half metallic conductor. In Figures 2b the bands for one spin cross the Fermi level while bands of the opposing spin show a large band gap across the Fermi level, thus indicating that these materials will be half metals.



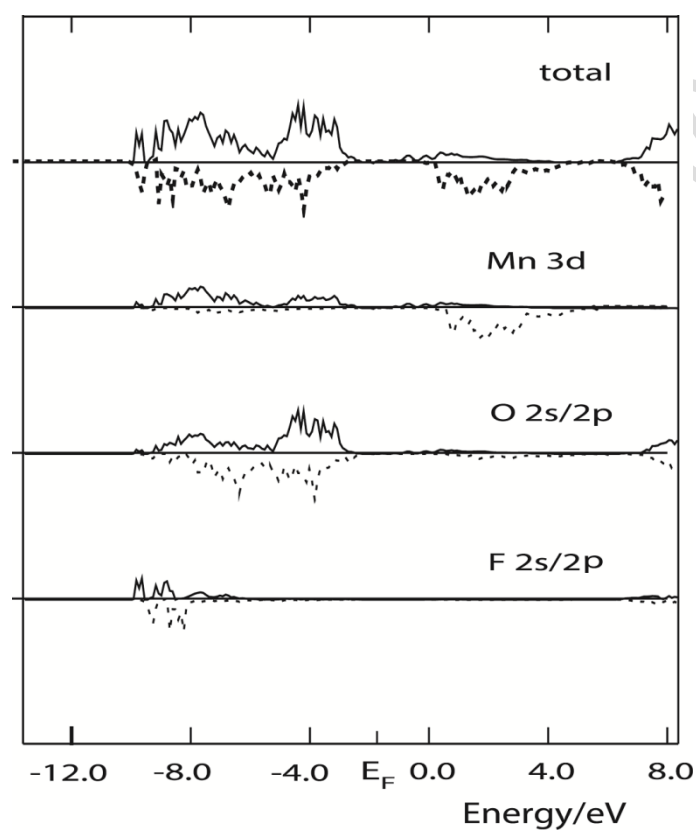
a)



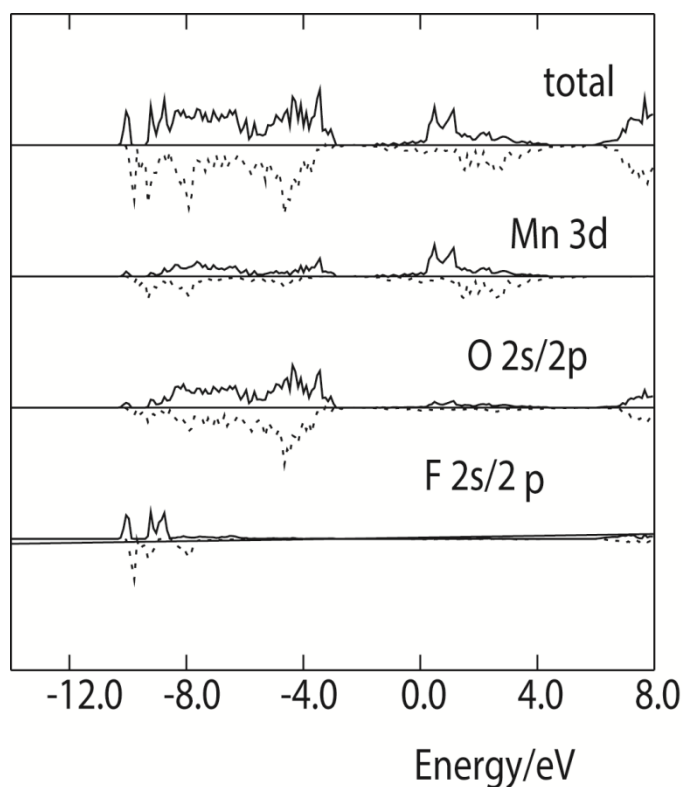
b)

Figure 2: Band structure of $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ a) the ferromagnetic state of model A, b) the ferromagnetic state of model B. Bands of one spin are indicated by darker lines and those of the other spin by lighter lines. $1\text{eV} = 1.602677 \times 10^{-19} \text{ J}$

Figure 3 shows the density of states for the ferromagnetic state of the two models.



a)



b)

Figure 3: Total density of states and projections of Mn, O and F for a) the ferromagnetic state of Model A, and b) the ferromagnetic state of Model B. $1\text{eV} = 1.602677 \times 10^{-19} \text{ J}$

For the ferromagnetic state of model A (Figure 3a), the highest occupied alpha spin band has contributions from 3d orbitals on both manganese ions and 2p orbitals on oxygen. The lowest unoccupied band has contributions from 2p on oxygen and 3d on only the Mn^{3+} ion. The highest occupied beta spin band is a purely oxygen band, whereas the lowest unoccupied band is composed entirely of manganese 3d orbitals on the Mn^{3+} ion. The density of states just below the Fermi level is higher for the alpha electrons than that for the beta electrons. The lowest unoccupied band for the alpha electrons starts at lower energies than the lowest unoccupied band for the beta electrons. The energy gap between the highest occupied level and the lowest unoccupied level is 0.440 eV for the alpha electrons and 2.27 eV for the beta electrons. Assuming equal densities of states the ratio of alpha to beta electrons excited across this gap at 298 K is about 50:1. However the density of states for the alpha electrons is higher than that of the beta electrons towards the top of the highest occupied band and this would increase the proportion of current carried by alpha electrons.

The density of states around the Fermi level in the half metallic model B (Figures 3b) is low indicating that there is a low density of charge carriers in these materials. Inspection of the band composition of the current carrying-spin in the ferromagnetic state of model B shows that the bands crossing the Fermi level are predominantly formed from Mn d e_g orbitals and O 2p_z. Both manganese ions in the unit cell contribute to these bands.

4. Discussion

In model A, both manganese ions are surrounded by five oxide and one fluoride ions. Valency rules dictate that either one manganese ion is in oxidation state +3 and the other in oxidation state +4 or that, by sharing electrons, both ions achieve an electron density equivalent to an oxidation state of +3.5. Our results indicate that in the lower energy model, the manganese ions adopt different oxidation states, although there is evidence of some electron transfer such that the ion in oxidation state +3 has a lower than expected value for the difference in spin up and spin down densities and the +4 state has a higher than expected value. The distinction between the oxidation states of the two manganese ions leads to differences in the geometry of the octahedron of anions surrounding the ions. While the equatorial Mn-O distances are constrained by the overall crystal structure to be similar for the two ions, there is a marked difference in the Mn-F distances and the apical Mn-O distance with both these distances being shorter for Mn⁴⁺. The geometry around both these ions is thus a distorted octahedron. We predict this compound to be small band gap semiconductor. It should be noted however that the band gap is small only for spins of one type, so that the current will be dominated by carriers of one spin type. This could prove useful in spintronic devices such as spin-biased transistors.

Model B has a layered structure with manganese ions alternately surrounded by six oxide ions and four oxide plus two fluoride ions. Its ground state is a ferromagnetic half metal. It could be considered effectively as composed of alternate layers of SrMnO₃ and SrMnO₂F and it might thus be expected that the SrMnO₃ layer would be where conduction occurs. Interestingly despite the layer structure, both manganese ions in the unit cell contribute to these bands. Thus we predict the conductivity will be three dimensional rather than confined to a layer. This indicates that the material will not be a two-dimensional conductor but supports strong coupling of the spins on these ions through the oxide ions via double exchange. Such a band structure is characteristic of manganites exhibiting CMR. This material is a possible candidate for CMR but it is accepted that electronic and magnetic nanoscale phase separation is crucial for this property[see for example 32]. Monte Carlo and/or molecular dynamics calculations would be needed to explore the distribution of different phase nanoscale structures. While it is expected that, experimentally, the product of a solid state synthesis would have a structure based on Model A, possibly with some randomisation of fluorine substitution, it may be possible to use CVD, for example, to obtain a structure based on Model B.

Spins on adjacent manganese ions are more strongly ferromagnetically coupled in model B than in model A. We therefore suggest that a compound with the structure of Model A will have lower Curie temperature than one with the model B structure.

Conclusion - DFT calculations on models of Sr₂Mn₂O₅F suggest that the lowest energy form of this material is a ferromagnetic semiconductor with a structure in which each manganese ion is surrounded by one fluoride and five oxide ions. It is predicted to possess a small band gap for only one type of spin and could therefore act as a spin-biased semiconductor. A higher energy form with a layer structure in which manganese ions in successive layers were

surrounded by six oxide ions and by four oxide ions and two fluoride ions was also investigated. This is predicted to have a ferromagnetic half metallic ground state and is a possible CMR candidate, although in practice, other factors may prevent it displaying this property. Extensive Monte Carlo or molecular dynamic calculations would be needed to investigate this possibility theoretically.

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Highlights

- $\text{Sr}_2\text{Mn}_2\text{O}_5\text{F}$ has been identified as having potential for electronic devices.
- This structure is predicted to be a spin-biased ferromagnetic semiconductor.
- Properties are varied by anion- doping rather than the more common cation-doping.
- Mn is surrounded by a distorted octahedron of five oxide and one fluoride ions.